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Vol. 29. No. 240. December 1943.

SYNTHETICS FOR THE PETROLEUM INDUSTRY.

By E. A. Evans (Member of Council).

A wide field is being uncovered by the aid of organic synthesis. Part of the area has been exhibited in the paper which Dr. Dunstan presented in March, 1943. Another view will be revealed in this paper. The two subjects may look very different from each other, but nevertheless both remain structural patterns from which the modern petroleum industry is being built. The naturally occurring petroleum hydrocarbons have been subjected to condensations, alkylations, and rearrangements to achieve definite results. Sometimes the success sought cannot be reached by systematic organic chemistry, consequently another avenue in this science must be explored. The two approaches may seem dissimilar, but in fact they are closely co-ordinated. They may be regarded as two of the components needed for the formation of the complex whole.

A very useful contribution to the science of petroleum has been given by the workers on chemical addition agents. The synthetic compounds which they have prepared have enabled notable victories to be won. Perhaps the most widely known additive is tetraethyl lead. Certainly its application to fuel research for the internal-combustion engine has had immense influence on the development of the I.C. engine and the affairs of man. It has now become so commonplace that we cease to marvel at it, but tetraethyl lead is only one of the organic compounds which have been used to solve problems confronting the petroleum industry. It is with these compounds that this paper deals.

The stimulus to expand the list of additives is the need to check oxidation and corrosion and to increase film strength. By looking at the long list of suggested compounds to meet these needs it will be seen that the solutions to the problems can be met in a great variety of ways, or, alternatively, there may be much conflict of opinion upon the respective merits of the individual additives. Probably both are true. The use of additives is practised in many phases of the petroleum industry, and is likely to grow.

In this paper it would be out of place to attempt any review of the economics of the petroleum industry, but it can be said that the use of anti-oxidants in petrols has contributed to the low tax-free price. Although tetraethyl lead is described as an anti-knock compound, it is an anti-oxidant by virtue of its ability to reduce the very high rate of oxidation at very high temperatures. But oxidation reduction rates at high temperatures are not the only problems associated with petrol. Gum formation and oxidation at atmospheric temperatures have to be delayed. The response to chemical addition agents varies, but the most effective additives contain hydroxyl or amino-groups. Of the compounds whioh have been used are pyrogallol, catechol, α-naphthol, *p*-phenylenediamine, *p*-aminophenols, and benzyl *p*-aminophenol. The anti-oxidant delays oxidation by extending the induction period, or by destroying metallic or other pro-oxidation catalysts. Among the compounds which have been suggested for neutralizing pro-oxidants may be mentioned disalicylethylenediamine. It is claimed to be capable of nullifying the effect of copper or copper salts.

To prevent the darkening of the colour of petrol, tributylamine and triamylamine are recommended. Whether the anti-oxidants react with peroxides or molecular oxygen is not known.

To obtain a conception of the vast amount of work which has been conducted upon chemical addition agents it is necessary to turn to the patent literature. Unfortunately this class of literature leaves much to be desired, because it aims at making claims, and only refers to the chemistry and behaviour of the substances sufficiently to uphold the claims. Synthesis being the immediate interest, it is permissible to do scant justice to anything lying outside its ambit. So an endeavour will be made to classify the reactions involved to illustrate the types of compounds which have been made or suggested.

Synthesis by the direct addition of one or more atoms to a compound is theoretically the simplest chemical reaction, and should therefore be considered first. Some addition reactions are so simple that they occur with almost explosive violence, others need a little encouragement, but some demand much persuasion.

Hydrogen can be added by the simple expedient of treating a responsive compound with acid and a metal, or sodium and alcohol. But the great hydrogenation industry is built upon the forceful entry of hydrogen into an organic compound under the influence of heat, pressure, and a catalyst. The well-known conversion of unsaturated liquid glycerides into saturated solid glycerides by molecular hydrogen is a notable example of hydrogenation.

$$\begin{matrix} CH_2\cdot OOC\cdot(CH_2)_7\cdot CH{=}CH\cdot(CH_2)_7\cdot CH_3 \\ CH\cdot OOC\cdot(CH_2)_7\cdot CH{=}CH\cdot(CH_2)_7\cdot CH_3 \\ CH_2\cdot OOC\cdot(CH_2)_7\cdot CH{=}CH\cdot(CH_2)_7\cdot CH_3 \end{matrix} + 3H_2 \xrightarrow{\text{catalyst}} \begin{matrix} CH_2\cdot OOC\cdot(CH_2)_{16}\cdot CH_3 \\ CH\cdot OOC\cdot(CH_2)_{16}\cdot CH_3 \\ CH_2\cdot OOC\cdot(CH_2)_{16}CH_3 \end{matrix}$$

Oxygen is imparted to unsaturated compounds by the usual oxidizing agents. So far the direct-oxidation products have not claimed greater attention than as starting-points for further treatment. The addition of oxygen can be carried to the stage of the peroxide. Whilst it is true that many peroxides are exceedingly unstable, there are many which are easily made through the medium of sodium peroxide, although it is well known that benzaldehyde is oxidized by contact with air in the presence of acetic anhydride to acetyl benzoyl peroxide, $C_6H_5\cdot CO\cdot O\cdot O\cdot CO\cdot CH_3$. The only peroxide which seems to have been offered to the petroleum industry is tetrahydronaphthalene peroxide to inhibit the staining of copper by lubricating oils.[1]

Sulphur will add on to many unsaturated compounds at temperatures above its melting point. The reaction is so easily undertaken that sulphurization of cracked wax, fatty oils, fatty acids, etc., is performed on a large scale for the preparation of cutting oils and sulphur-containing lubricants. The sulphur probably adds on at the point of unsaturation.[2,3,4,5] By their nature these bodies are composed of an array of sulphur-containing compounds the composition of which is vaguely known and difficult to control.

$$R\cdot CH{=}CH\cdot R + 2S \longrightarrow R\cdot \underline{CH\cdot S\cdot S\cdot CH}\cdot R$$

To obtain a comparatively pure compound by addition methods divinyl-

acetylene is heated with hydrogen sulphide under pressure, when the sulphur is freed and attaches itself at the double bond.[6]

Chlorine will combine additively with nearly all ethylenic compounds to give chlorine-substituted saturated compounds. It will also react with saturated hydrocarbons if aided by a catalyst. By the chlorination of oleic acid at moderate temperatures dichlorostearic acid is produced, which when converted into its calcium salt has found widespread use as a detergent in lubricating oils for some diesel engines.[7] Aromatic hydrocarbons can also

$$\begin{matrix} CH\cdot(CH_2)_7\cdot CH_3 \\ \| \\ CH\cdot(CH_2)_7\cdot COOH \end{matrix} + Cl_2 \longrightarrow \begin{matrix} Cl\cdot CH\cdot(CH_2)_7\cdot CH_3 \\ | \\ Cl\cdot CH\cdot(CH_2)_7\cdot COOH \end{matrix}$$

be induced to add on chlorine, yielding, for example, benzene hexachloride. Naphthalene tetrachloride crystallizes quite readily when chlorine is passed through a chloroform solution of naphthalene, even at room temperature. This compound

$$C_{10}H_8 + 2Cl_2 \longrightarrow C_{10}H_8Cl_4$$

is particularly useful when it is desirable to raise the film strength of an internal combustion engine lubricating oil without affecting the other properties of the oil.[8]

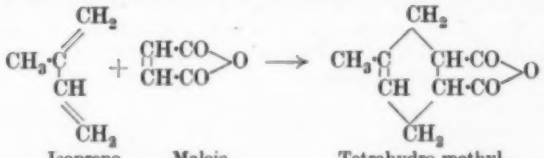
Sulphur Chloride has the power of adding both sulphur and chlorine simultaneously to the same molecule, the advantage being that frequently the combined efforts of sulphur and chlorine are greater than the efforts of either of them. Extreme-pressure bases for admixture with mineral oil have been made by treating fatty oils with sulphur mono-chloride.[9]

$$2{>}C{:}C{<} + S_2Cl_2 \longrightarrow \begin{matrix} {>}CCl\cdot C{<} \\ | \\ {>}CCl\cdot C{<} \end{matrix} S + S$$

This type of compound is elegantly converted into a hydroxy-compound by removing the chlorine by hydrolysis.[10]

Phosphorus Halides and Sulphides such as phosphorus trichloride, PCl_3, and phosphorus pentasulphide, P_2S_5, behave in an analogous way to the sulphur chlorides.[11]

Diels Alder reaction between unsaturated compounds such as quinones, unsaturated aldehydes, acids, lactones, and their esters with compounds containing conjugated double linkages, of which butadiene and isoprene are examples, is another type of addition. In this reaction the two substances when heated together in a solvent unite to form a six-membered



Isoprene — Maleic anhydride — Tetrahydro-methyl-phthalic anhydride

ring. The resultant lactone yields the corresponding acid which can be esterified.[12] Probably by the interaction of a long-chain alcohol considerable oiliness properties can be obtained. Just what advantage a tetrahydro-phthalic anhydride construction has over phthalic anhydride

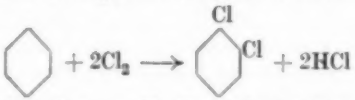
is not clear, as diethyl phthalate has quite a distinct film-strength characteristic.

Sulphuric Acid may conveniently be taken in this group when considering the sulphonation of unsaturated complex petroleum constituents. The addition of $\cdot SO_3H$ gives rise to petroleum sulphonic acids, or the so-called mahogany acids. When they are combined with sodium they are regarded almost as an essential ingredient of soluble oil. Their heavy metal salts have found favour as detergents and anti-oxidants.[13, 14]

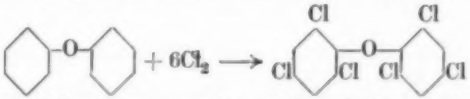
Perchloromethyl Mercaptan, $CSCl_4$, has been proposed as a reactant with unsaturated organic compounds, *e.g.*, cracked waxes, etc.[15]

Substitution or the preparative work of exchanging a hydrogen atom for a chlorine or a sulphur atom, or perhaps a specific group, has yielded a number of compounds which in themselves have direct application, or form the basis for other syntheses.

Chlorine.—The chlorinated saturated long-chain hydrocarbons, found in paraffin wax, have found a ready market for incorporation in cutting oils and hypoid lubricants, and a still more extended use for them is envisaged. The substitution of chlorine in the aromatic nucleus is effected by treating benzene with chlorine in the presence of the carrier iodine, giving, amongst



other things, *o*-dichlorobenzene.[16] By chlorinating diphenyl ether, as many as six chlorine atoms can be introduced into the molecule.[17]

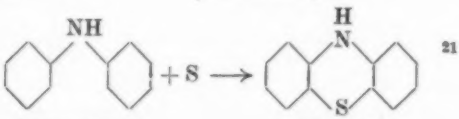


A mixture of *o*-dichlorobenzene and hexachloro-diphenyl ether is stated to be a sludge disperser, whereas the hexachloro-compound by itself is a mild extreme-pressure additive.

Of the many chloro-compounds which have been made, chlorinated dibenzyl disulphide and chlorinated methyl stearate are worthy of special notice.[18, 19]

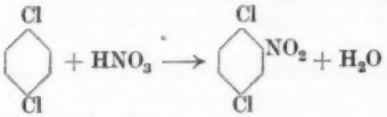
Sulphur displacement of hydrogen has not produced any compounds of outstanding merit. The contribution of aniline disulphide and phenthiazine to the list of possible anti-oxidants is of interest, because in each case the sulphur is bridging the two benzene rings and the nitrogen in the two compounds is differently attached.

Aniline — Aniline disulphide [20]



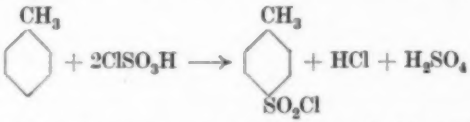
Diphenylamine — Phenthiazine [21]

Nitration.—The activation of chlorine by substituted nitro-groups is noticeable when one nitro-group is introduced, and is maintained on the introduction of a second,[22] provided they are not in the *o*-position to the same chlorine atom. Nitro-*p*-dichlorobenzene possesses mild extreme-



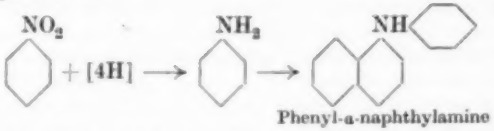
pressure properties, but in 1 : 4-dichloro-2 : 6-dinitrobenzene they are void. Nitration has also been applied to arylamines.[23]

Sulphonation is a variation of sulphur substitution. By participation of chlorosulphonic acid aromatic hydrocarbons are converted into aryl sulphonyl chlorides.[24, 25] In this case there is both sulphonation and



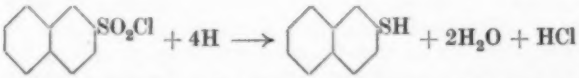
halogenation. The dual presence of sulphur and chlorine almost automatically puts the compound into the extreme-pressure category.

Reduction of some of the substituted compounds has led to the discovery of at least one very promising anti-oxidant. Nitrobenzene when reduced with iron and hydrochloric acid yields aniline, which readily attaches to itself a naphthalene ring when heated with α-naphthol in the presence of a little sulphuric acid.



Phenyl-α-naphthylamine

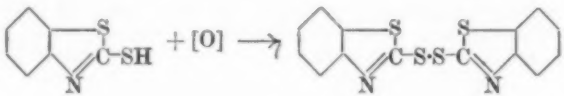
Sulphonyl chlorides furnish a useful transition from compounds in the E.P. classification to those in the anti-oxidant class by simple reduction. β-Naphthyl sulphonyl chloride forms β-naphthyl mercaptan when treated with zinc and acetic acid.[27]



Oxidation opens a field of almost unlimited possibilities in the search for synthetic compounds useful to the petroleum industry. Only the fringe is being explored, but in it there are already available oiliness agents

and pour-point depressants. The oxidation of petroleum hydrocarbons produces a dazzling array of alcohols, aldehydes, ketones, lactones, and acids, all possible starting-points for productive research. Until recently the oiliness compounds were sought among the glycerides of naturally occurring oils and fats, but to-day they are being manufactured from long-chain alcohols and acids, and marketed in the form of synthetic esters.[28, 29]

Oxidation is not restricted to the mere attachment of oxygen to a receptive molecule. The active oxygen atom can be instrumental in deforming a molecule by detaching from it an atom or even a group; in fact the situation can arise that by the abstraction of a single atom the residual part of the molecule is driven to condense with another residual part. This situation is taken advantage of in the transformation of a mercaptan, to a disulphide. When mercaptobenzothiazole is oxidized under the influence of ferric chloride, the hydrogen in the mercaptan-group is oxidized, and condensation follows at the free valency of the remaining sulphur atom.[30]



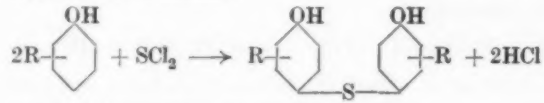
It is convenient to mention here that the solubility of possible additives in petroleum oils should be considered at an early stage in the research programme. Many compounds which have been suggested have lost much of their original novelty through their limited solubility. Sometimes their insolubility can be obviated by resort to a mutual solvent. But it is probably better to attach a group which will increase the solubility of the parent compound.

Stability is equally important. It is not necessary to define quantitatively the degree of stability for compounds in general, although compounds for specific purposes must be adaptable to the needs imposed upon them. For most hypoid gear lubricants it is necessary that the compound when dissolved in oil shall withstand repeated heatings to 150° C. for no other reason than that the maximum oil temperature in a rear axle never exceeds 135° C. It is recognized that temperatures far in excess of 135° C. are momentarily attained on the gear surfaces, consequently the time factor may become an essential consideration. A constant cascading of oil at approximately 60° C. in a turbine provides ample opportunity for oxidation at a comparatively low temperature. The highly mobile film with the interaction energy of the dissolved oxygen operating for year after year casts a responsibility on an anti-oxidant of no mean order. The effect of the bombardment by the neighbouring oxygen on the oil must be repelled by the additive. Internal-combustion engines present another set of conditions, of which the heat factor is probably the most dangerous. In the piston ring area the oil may be exposed to temperatures up to 600° F., and even be cast on to vacant sites. How the anti-oxidant behaves in this area nobody knows. We do know, however, that some compounds inhibit the oxidizing influence of the iron, its oxides, or its compounds, and others

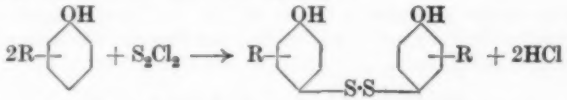
delay the latent period of oxidation of the oil. The fact emerges that the anti-oxidant must resist very high temperatures.

The replacement of hydrogen activated by electronegative groups is possible by treatment with sulphur monochloride, sulphur dichloride, or thionyl chloride. This reaction is taken advantage of in the synthesis of thioethers and certain polysulphides.

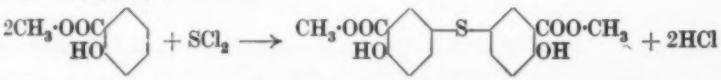
When phenols in a solvent—*e.g.*, carbon tetrachloride—are treated with sulphur dichloride, the hydrogen in the *p*-position is easily displaced, giving rise to an aryl hydroxy-thioether,



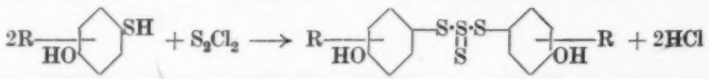
or with sulphur monochloride a disulphide,[31]



Sulphur dichloride when reacted with hydroxy-esters—*e.g.*, methyl salicylate—in the presence of a metal catalyst yields di-(3-carbomethoxy-4-hydroxy phenyl) thioether.[32]

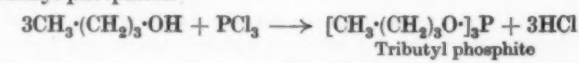


Then there is the possibility of removing the hydrogen from the electronegative groups themselves by the action of sulphur mono- and di-chlorides on mercaptans for the building up of tri- and tetra-sulphides respectively.[33]



By replacing the sulphur chlorides by phosphorus trichloride a series of phosphorus-containing compounds can be prepared.

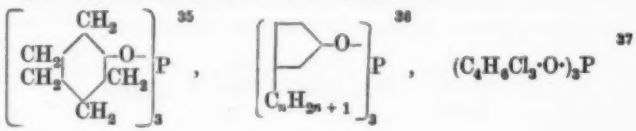
Action on alcohols in the presence of pyridine or other acid binding agent gives trialkyl phosphites.[34]



Tributyl phosphite

Tributyl phosphite is used to protect cadmium alloy bearings against oil acid attack.

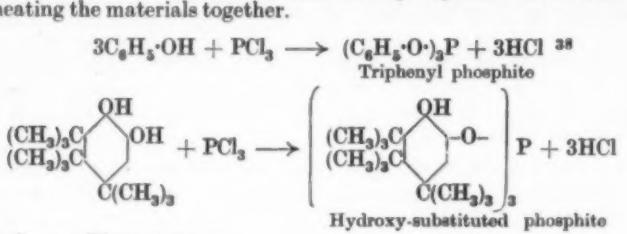
Similarly, phosphites are made from *cyclo*hexanol, naphthenyl alcohols (from naphthenic acids), and trichlorobutyl alcohol.



Action on Phenols.—Phenols react with phosphorus trichloride merely on heating the materials together.

$$3C_6H_5{\cdot}OH + PCl_3 \longrightarrow (C_6H_5{\cdot}O{\cdot})_3P + 3HCl$$ [38]

Triphenyl phosphite



[39]

Hydroxy-substituted phosphite

Action on Mercaptans.—

$$3C_5H_{11}{\cdot}SH + PCl_3 \longrightarrow (C_5H_{11}S)_3P + 3HCl$$

The reaction proceeds smoothly both with aliphatic and aromatic mercaptans, resulting in alkyl and aryl thiophosphites.[40, 41, 42, 43]

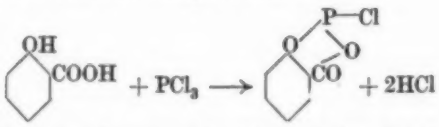
Action on Tertiary Alcohols.—The aim to synthesize a stable compound containing useful phosphorus and chlorine was not simply attained. Phenols will produce phosphorus dihalides, but they are unstable and totally unsuitable for lubrication.

$$C_6H_5{\cdot}OH + PCl_3 \longrightarrow C_6H_5OPCl_2 + HCl$$

From tertiary aromatic alcohols the goal can be won by stabilizing with several aryl groups.[44]

$$(C_6H_5)_3C{\cdot}OH + PCl_3 \longrightarrow (C_6H_5)_3COPCl_2 + HCl$$

Action on o-Hydroxy Acids.—This last development is further exemplified in the synthesis of *o*-phosphito-benzoyl chloride.[45]



The union of this type of compound with alcohols, phenols, amines, etc., by displacement of the chlorine atom gives rise to some new and interesting derivatives of phosphorus. Doubtless the stabilizing in the former case is due to the extra weight of the multiple phenyl groups, and in the latter to the heavy group attached to the benzene ring.

Action on Ammonia and Amines.—In the extension of the study of phosphorus compounds the action of phosphorus trichloride on alkyl and aryl amines has not been overlooked.[46]

$$6(C_5H_{11})_2NH + PCl_3 \longrightarrow [(C_5H_{11})_2N]_3P + 3(C_5H_{11})_2NH{\cdot}HCl$$

A striking contribution comes from the discovery that the three groups attached to the phosphorus need not necessarily be the same, but can be derived from an amino, hydroxy or mercapto compound.[47]

$$\begin{matrix} A{\cdot}NH_2 \\ B{\cdot}OH \\ C{\cdot}SH \end{matrix} + PCl_3 \longrightarrow \begin{matrix} A{\cdot}NH \\ B{\cdot}O \\ C{\cdot}S \end{matrix} \!\!> P + 3HCl$$

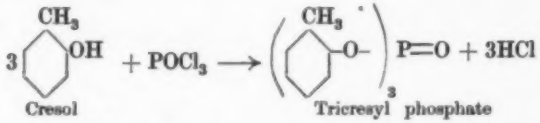
Just as the phosphites are prepared from phosphorus trichloride, so the phosphates are prepared from phosphorus pentachloride or phosphoryl chloride.

Action on Alcohols.—Almost any alkyl phosphate can be made by the action of phosphoryl chloride on aliphatic alcohols.

$$3C_4H_9{\cdot}OH + POCl_3 \longrightarrow (C_4H_9{\cdot}O{\cdot})_3P{=}O + 3HCl$$

Chlorinated alkyl phosphates are equally well prepared, and even a phosphate from castor oil.[48, 49, 50, 51]

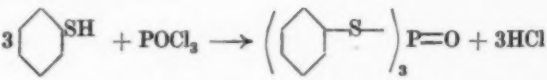
Action on Phenols.—



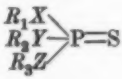
Cresol — Tricresyl phosphate

Tricresyl phosphate was one of the pioneer compounds suggested to meet the needs of extreme-pressure lubrication.[52] About the same time chlorinated aryl phosphates and compounds like tri-*p*-ethyl phenyl phosphate were introduced.[53, 54]

Action on Mercaptans.—



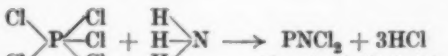
These alkyl and aryl thiophosphates may subsequently be halogenated. Thiophosphates of a very mixed type have also been successfully synthesized.[55]



where R_1, R_2, R_3 = alkyl or aryl groups

X, Y, Z = oxygen or sulphur

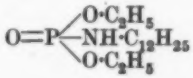
Action on Ammonia and Amines.—



Phosphonitrilic halide

$$C_{12}{\cdot}H_{25}{\cdot}NH_2{\cdot}HCl + POCl_3 \longrightarrow O{=}P(Cl)(Cl)(NH{\cdot}C_{12}H_{25}) + 2HCl$$

The phosphonitrilic halides can be extended in length and complexity by polymerization and condensation with alcohols, phenols, mercaptans, etc.[56] The long-chain phosphonamide is claimed to have added advantages if the phosphorus is linked to ethoxy-groups.[57]

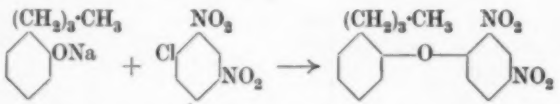


Syntheses involving the removal of metal atoms.

From Phenates.—By application of the Williamson synthesis

$$R{\cdot}ONa + R'X \longrightarrow R{\cdot}O{\cdot}R' + NaX$$

alkyl phenyl oxy-ethers of 2 : 4-dinitrobenzene have been prepared for use as mild extreme-pressure agents.[58]



The method has been successfully employed with alkali phenates and chlorinated paraffin wax.[59]

From Alkali Sulphides, Disulphides, etc.—By the interaction of benzyl chloride and sodium disulphide dibenzyl disulphide is produced.[60]

Chlorinated wax will also react with sodium sulphide in such a way that a part of the whole of the chlorine will be removed, yielding a long-chain compound bridged by sulphur.[61]

From Alkali Cyanides, Thiocyanates, etc.—The linking of a sulphur atom on to the side-chain of a benzene nucleus can be accomplished by treating benzyl chloride with sodium thiocyanate.

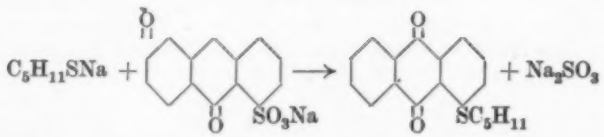
$$C_6H_5{\cdot}CH_2Cl + NaCNS \longrightarrow C_6H_5{\cdot}CH_2{\cdot}CNS + NaCl$$

Of the various thiocyanates suggested as mild extreme-pressure agents should be mentioned the higher alkyl thiocyanates and *iso*thiocyanates. Also the reaction products containing a thiocyanate group and chlorine atoms resulting from the reaction between alkali thiocyanates with chlorinated hydrocarbons. Ethylene cyanide alone has even been included in the list.[62, 63, 64]

From Alkali Mercaptides.—The use of alkali mercaptides follows almost in natural sequence. Specific cases of the general reaction occur when

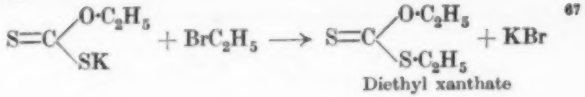
$$R{\cdot}Cl + R'CH_2SNa \longrightarrow R{\cdot}S{\cdot}CH_2R' + NaCl$$

n-butyl and amyl mercaptides are condensed with chlorinated hydrocarbons. When *n*-amyl mercaptide acts upon alkali α-anthraquinone sulphonates an analogous reaction takes place.[65, 66]

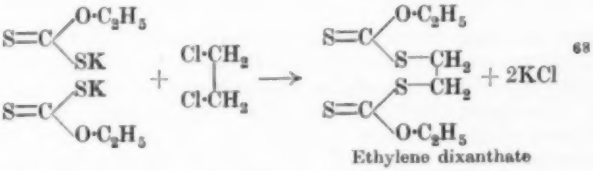


From Alkali Xanthates.—Starting with potassium ethyl xanthate

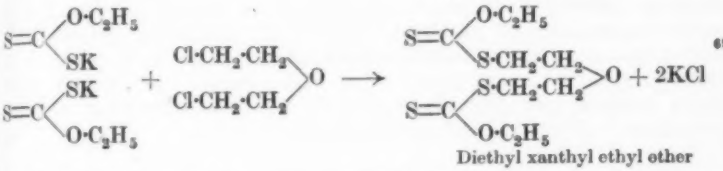
a series of compounds can be synthesized having extreme-pressure properties.



Diethyl xanthate

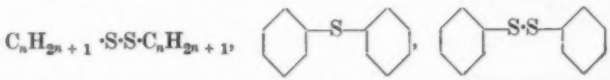


Ethylene dixanthate

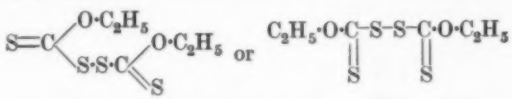


Diethyl xanthyl ethyl ether

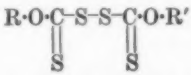
Before advancing it is necessary to deflect slightly to a patent which claims alkyl mono- and di-sulphides, and aryl mono- and di-sulphides.[70]



This invention of using an alkyl disulphide reveals the possibility of combining two thiocarbonate radicals to produce xanthic disulphides. Although these compounds are mentioned in the patent specification, they do not appear in the claims.

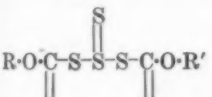


The rearrangement of the grouping in the formula is given because the use of bis-alkyl xanthogen has been patented.[71]



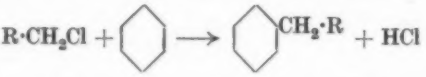
RR′ = alkyl or aralkyl radicals

Having succeeded in introducing two atoms of sulphur into a molecule, and then four, it caused no surprise to see the announcement of xanthogen tetrasulphide which contains six.[72]



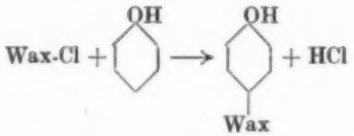
RR′ = alkyl, aryl, aralkyl or *cyclo*alkyl radicals

Friedel and Craft's reaction, when introduced in 1877, was applied to the formation of alkylbenzenes through the interaction of alkyl halides with benzene in the presence of anhydrous aluminium chloride.

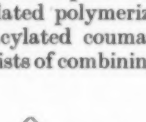


Since then the scope of the reaction has been considerably enlarged, and has assumed a value of considerable importance in the synthesis of a number of compounds particularly useful as pour-point depressants.

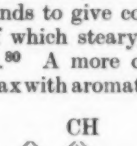
With Chlorinated Hydrocarbons.—The condensation of chlorinated paraffin wax with aluminium chloride, and the treatment of the polymerization products of *iso*butylene with sulphur monochloride, may not be within the spirit of the Friedel and Craft reaction, but they are linked to it by the application of the condensing agent, aluminium chloride.[73, 74] More orthodox are the condensation of chlorinated wax with ethers, such as diphenyl oxide,[75] or with phenols,[76] or with phenols, acids, ethers, thioethers, ketones, and then converting the products into their metallic derivatives,[77] or with the aryl ethers and thioethers.[78]



With Acyl Halides.—By the aid of acyl chlorides, R·CO·Cl, long chains can be added to complex aromatic compounds to give compounds of the nature of acylated polymerized indenes, of which stearyl indene [79] is an example, or acylated coumarone polymers.[80] A more complicated condensation consists of combining chlorinated wax with aromatic hydrocarbons,



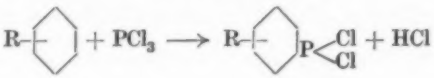
Indene



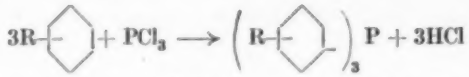
Coumarone

and further condensation with dicarboxylic acid halides—*e.g.*, phthalyl chloride.[81] The condensation of naphthenyl halides with aromatic petroleum extracts [82] will come as a special item of interest to those who are in petroleum refineries. All these large molecule compounds are offered as pour-point depressants, viscosity-index improvers, or oiliness agents.

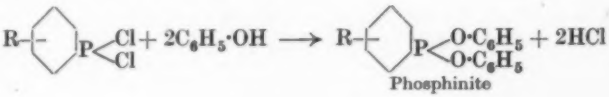
With Phosphorus Halides and Related Halides.—Alkyl benzenes will react with phosphorus trichloride under the influence of aluminium chloride to give alkyl benzene dichlorophosphines,[83]



or in the presence of an excess of hydrocarbon aryl phosphines.[84,85,86] By a suitable choice of material phosphine oxides and sulphides have been synthesized.

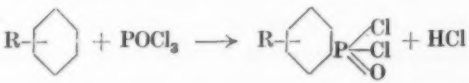


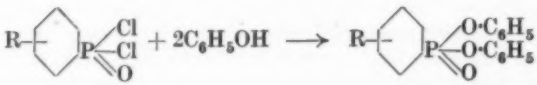
Phosphinites are obtained by the reaction of dichlorophosphines with phenols, alcohols, etc.[87]



Phosphinite

In an analogous manner, phosphoryl chloride will react with aromatic hydrocarbons in presence of aluminium chloride, and the product when treated with an alcohol or phenol yields a phosphinate.





Phosphinate

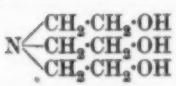
Less definite compounds arise when $PSCl_3$ acts upon lubricating oil stocks.[88] Arsenic and antimony are alternatives to phosphorus in this series of compounds, as we see in such a compound as triphenyl arsine sulphide, made by heating triphenyl arsine with sulphur,[89] or triphenyl stibine.[90]

Other Condensation Reactions.—Most of these condensations are based upon well-established processes. Carboxylic acids will react directly with the hydroxyl group of an alcohol to yield acyl derivatives. The reaction

$$R{\cdot}COOH + HO{\cdot}R' \longrightarrow R{\cdot}COOR' + H_2O$$

is restricted to primary and secondary alcohols, but polyhydric alcohols condense with polycarboxylic acids.[91]

The condensation of ammonia with aliphatic alcohols has given us the valuable ethanolamines and their fatty acid salts and esters.[92]

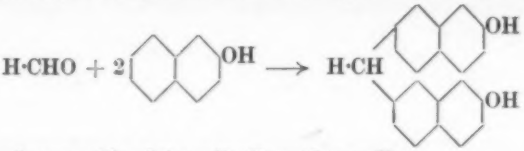


And lastly the condensation products of aldehydes with polyhydric alcohols[93]

$$R{\cdot}CHO + 2R'OH \longrightarrow R{\cdot}CH(OR')_2 + H_2O$$

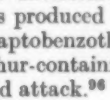
Acetal

with phenols to give compounds such as methylene di-β-naphthol,[94]

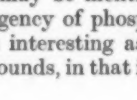


and with hydroxy-acids of the salicylic acid type.[95]

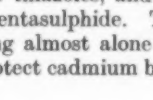
Of the unclassified types may be mentioned the thiazoles, and all the products produced by the agency of phosphorus pentasulphide. The use of mercaptobenzothiazole is interesting as standing almost alone among the sulphur-containing compounds, in that it will protect cadmium bearings from acid attack.[96]



Thiazole



Benzothiazole



Mercaptobenzothiazole

Products finding application mainly in the extreme-pressure field may be obtained by the action of phosphorus penta- or sesqui-sulphides on a variety of materials including alcohols and mixtures of alcohols, wherein at least one possesses a straight chain of eight or more carbon atoms,[97, 98] unsaturated fatty oils, and primary and secondary aliphatic or aromatic amines,[99] and on mixtures of synthetic secondary and tertiary alkylated phenols.[100] Other products suitable as oxidation and corrosion inhibitors have been prepared by the action of these phosphorus sulphides on alcohols and phenols,[101] and on mixed naphthenyl alcohols.[102]

Compounds of metals were advocated as far back as 1887.[103] Many years later metallic stearates were patented for use in castor oil,[104] but it was not until 1926 that any comprehensive publication was made on the value of metallic soaps in mineral oils.[105] Since then there has been almost a flood of compounds containing metal ions.

From Acids.—By the simple process of neutralizing an alkaline solution with a fatty acid, and adding thereto an aqueous solution of a soluble metallic salt, a metallic soap is precipitated. Oleates of lead,[106] tin,[107] chromium,[108] and mixtures of chromium and tin [109] or nickel [110] have all been applied to mineral oils. Naphthenates of calcium,[111] manganese, lead, zinc, copper, aluminium, and cobalt and tin [112] were natural sequences.

From Substituted Fatty Acids.—Soaps of sulphurized fatty acids,[113] chlorinated fatty acids (*e.g.*, calcium dichlorostearate),[114] and of fatty acids arylated at the double bond by means of aluminium chloride, of which phenyl stearic acid is an example, are extensions of the simple soaps. The calcium salt of phenyl stearic acid [115] has been mentioned specifically, and its other metallic salts in general.[116] The substituted stearic acid salts have been extended to include calcium chlorophenyl mercaptostearate,[117] and aluminium α-benzalstearate.[118] Soaps of the ether-substituted fatty acids are obtained by the action of sodium phenate on chlorinated fatty acids.[119]

From Other Acids.—The aluminium soaps of acids from oxidized sweated wax were doubtless prepared to obviate some of the difficulties encountered with aluminium oleate,[120] and metallic salts of wax-substituted aromatic acids and hydroxy-acids to provide very long-chain molecules.[121] Zinc di*iso*propyl salicylate [122] has been chosen from the metallic salts of alkylated aromatic carboxylic acids, probably because of its solubility in oil. The use of zinc is a little unusual. The recent appearance of soaps of rosin acids [123] and hydrogenated rosin acids [124] suggests that the non-substituted acid soaps may be finding new supporters.

Instead of using fatty acids combined with a metallic ion, it is possible to displace the hydrogen in a phenol to give a phenate or in a mercaptan to give a mercaptide. Most of the patented lubricant additives are made from alkali-insoluble phenols possessing alkyl chains by one of the following methods.

Action of Metallic Carbides on Phenols.

$$2R{\cdot}OH + CaC_2 \longrightarrow \begin{matrix} R{\cdot}O \\ R{\cdot}O \end{matrix}\!\!>\!Ca + C_2H_2$$

Direct Action of the Metal on the Phenol in an inert solvent.

$$6R{\cdot}OH + 2Al \longrightarrow 2Al(OR)_3 + 3H_2$$

Double Decomposition.—By dissolving the phenol in alcohol and converting it into the sodium phenate by adding sodium, and forming the derived metal salt by adding an alcoholic solution of the appropriate chloride.

$$2R{\cdot}OH + 2Na \longrightarrow 2R{\cdot}ONa + H_2$$

$$2R{\cdot}ONa + NiCl_2 \longrightarrow \begin{matrix} R{\cdot}O \\ R{\cdot}O \end{matrix}\!\!>\!Ni + 2NaCl$$

Direct reaction between the phenol and the hydroxide of an alkaline earth metal in an inert solvent—*e.g.*, benzene. The water formed is removed continuously.

$$2R{\cdot}OH + Ba(OH)_2{\cdot}8H_2O \longrightarrow \begin{matrix} R{\cdot}O \\ R{\cdot}O \end{matrix}\!\!>\!Ba + 10H_2O$$

Via Metallic Alcoholates.—Magnesium ethylate will react directly with a phenol to give a phenolate,

$$Mg(OC_2H_5)_2 + 2R{\cdot}OH \longrightarrow Mg(OR)_2 + 2C_2H_5OH$$

The long-chain substituted products appear again in this group as wax-substituted phenols and their derivatives,[125] metal alkyl phenates of the calcium cetyl phenate class,[126] and metallic derivatives of alkylated phenols containing nitro-, amino- or alkylamino-substituents.[127]

Similarly, the alcohols and thio-alcohols have been converted into metallic alcoholates and thio-alcoholates.[128, 129, 130]

True organo-metallic compounds are probably too expensive to be contemplated as chemical addition agents to lubricants in the present state of our knowledge. True, tetraethyl lead is used extensively in petrol,

but only a few ml. per gallon. The concentration of additives required for oils covers the range 0·07 to 10·0 per cent. Tetraethyl lead can be synthesized by the action of ethyl chloride on a lead–sodium alloy in the presence of water or alcohol and a catalyst, which may be pyridine. The Grignard reaction has been used for the preparation of tin tetrabutyl.[131] A

$$R{\cdot}Cl + Mg \xrightarrow[\text{ether}]{\text{dry}} R{\cdot}MgCl$$

$$4R{\cdot}MgCl + SnCl_4 \longrightarrow R_4Sn + 4MgCl_2$$

link with the thioethers is found in the organo-metallic compounds of bismuth, tin, or antimony used in conjunction with a hydroxy-substituted thioether. In an endeavour to increase the effectiveness of the metal it has been suggested that two atoms of metal joined together are better than one:[132]

$$(CH_3)_3SnNa + (C_6H_5)_3SnCl \longrightarrow (CH_3)_3Sn{\cdot}Sn(C_6H_5)_3 + NaCl$$

whereas other workers who support the idea of multiple atoms prefer to divide them.[133]

$$(CH_3)_3Sn(CH_2)_5Pb(CH_3)_3$$

Metallic Complexes.—The interest in organo-metallic compounds has been extended to the metallic complexes to be in keeping with the trend to explore in a general way the substances which are getting farther and farther away from those synthesized by simple chemical reactions. How far it is possible to go, and still remain within the economic field, is difficult to forecast. The probings into the unfathomable depths of organic chemistry must continue now that the pace has been set and the demand created. At times compounds are prepared and patented for specific uses, with little prospect of practical application within the petroleum industry, but which collectively provide the fragments of a picture from which a composite whole may ultimately be evolved, or a surprise arise. In this paper no attempt has been made to correlate structure with application. The author has already approached this subject in a previous paper (*J. Inst. Petrol.*, 1941, **27**, 165–187). The sole object of this discussion is to review, and classify, the compounds which have been patented as chemical addition agents for petroleum products, particularly lubricating oils.

Complex organo-metallic addition compounds are producible by interacting inorganic or organic metallic compounds, containing no free hydrocarbon radicals, with alkyl or aryl compounds of the elements in groups 5–6 right-hand columns, or with their acids or esters.[134]

$$Cu_2Cl_2{\cdot}(C_4H_9)_2S, \quad (C_{17}H_{33}{\cdot}COO)_2Ni(C_3H_7)_3PO_3$$

The preparation of extreme-pressure agents has been made by combining heavy metal compounds of alcohols, ketones, esters, and mercaptans with completely alkylated or arylated compounds of nitrogen, phosphorus, and sulphur, or alkyl or aryl phosphites.[135]

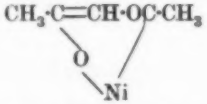
$$(CH_3)_3CSAg{\cdot}C_5H_5N$$

Cuprous butyrate diethyl sulphide [136] is an example of the class of complex

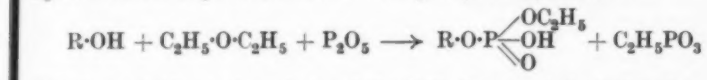
$$CuOOC{\cdot}C_3H_7{\cdot}C_2H_5{\cdot}S{\cdot}C_2H_5$$

resulting from metal oxides or hydroxides with (*a*) an organic compound containing replaceable hydrogen, and (*b*) an organic compound of group 5–6 with atomicity >1.

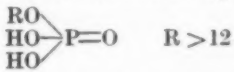
The multiplying instances of the application of nickel are further reflected in the β-diketone complex.[137]



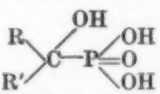
Metallic Phosphorus Compounds.—Some of the usefulness of the phosphorus atom is combined with the metallic atom by introducing them into the same molecular structure. This can be accomplished by refluxing higher alcohols or phenols in ether with phosphorus pentoxide.



The ether solution is decanted and the $C_2H_5{\cdot}O$ group is hydrolysed.



The resultant acid is dissolved in aqueous sodium hydroxide, and the calcium, magnesium, chromium, etc., salts prepared by precipitation. Calcium cetyl phosphate is prepared in this way.[138] A metallic alkyl phosphate can then be used in conjunction with a metallic alkyl phenate.[139] By treating nonadecane-2-one with phosphorus trichloride in acetic acid, and subjecting the sodium salt of the resulting acid to double decomposition, calcium 2-hydroxynonadecane-2-phosphonate can be obtained.[140]



Dialkyl 2-hydroxy phosphonic acid

In the petroleum industry special interest centres round the differences between pure petroleum products and those which are treated with chemical compounds. The ever-growing demand for less active and yet more active lubricants seems paradoxical, but we have to admit its truth. Lubricants must be resistant to enemy attack, whether it be by oxidation, pressure, or heat. The preferential destruction of part of the lubricant can be reduced by the imposition of barriers, and the more inert fractions have their feebleness of action countered by an intermingling of bodies of known chemical structure and activity. This aiding and abetting will continue until the treatment of petroleum products has advanced sufficiently to render the use of additives unnecessary.

My thanks are due to J. S. Elliott, M.A., for much valuable help.

C. C. Wakefield & Co., Ltd.,
Hayes, Middlesex.
C C

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THE INSTITUTE OF PETROLEUM.

A MEETING of the Institute was held at the Royal Society of Arts, John Adam Street, W.C.2, on Thursday, 29th July, 1943.

Mr. C. Dalley, President, occupied the Chair.

The following paper was presented :—

"Synthetics for the Petroleum Industry." By E. A. Evans (Member of Council) (see page 333).

DISCUSSION.

PROFESSOR GARNER, in opening the discussion, congratulated Mr. Evans on the presentation of a co-ordinated scheme from the mass of literature, particularly patent literature, on this subject of additives.

Apart from the reference to lead tetraethyl, most of the references given were to the lubricating oils, but there were a number of additives for fuels. Mr. Evans mentioned in the paper that the only peroxide which seemed to have been offered to the petroleum industry was tetrahydronaphthalene peroxide. There were, however, other peroxides which had been offered in connection with diesel fuels. It would be remembered that amyl nitrate and nitrite had been amongst the first substances suggested for improving the ignition qualities of diesel fuels, but in addition some of the organic peroxides, such as aldehyde or ketone peroxides, including acetone peroxide, had been suggested. (E.P. 428,972). These diesel fuel additives were required in proportions of 1 or 2 per cent, so they had not been extensively used for improving the ignition quality of diesel fuels, although they might be of value in connection with starting.

One rather interesting application in connection with lead tetraethyl, which had been brought out in a paper read before the *American Petroleum Institute* in 1940 (**21**, (III) 6), was the utilization of lecithin to improve the storage qualities of gasoline containing lead tetraethyl. Lecithin was a phosphatide and could be obtained by solvent extraction from soya beans; it was used in the proportion of 1 to 15 lbs. per thousand barrels. In the course of the discussion on that paper it was stated that a large group of glycerides such as corn oil or fish oil which had been activated by a suitable process, such as treatment with sulphur or ozone, could be used for the same purpose. A measure of the effect of these compounds in improving gasoline stability in sunlight had been given by the fact that 1 part to 40,000 might keep an unstable gasoline containing lead tetraethyl clear up to eight hours' exposure to sunlight, whereas otherwise it would become slightly cloudy in half an hour.

There was another interesting application, again on the fuel side rather than on the lubricating side, in connection with colour stability, and reference had been made in the paper to the fact that tributylamine and triamylamine were recommended to prevent the darkening of the colour of petrol. The discoloration of certain types of water white gasolines and kerosines when held in storage for prolonged periods had been a serious problem, and this type of colour stability in the dark was thus different from that mentioned above which was colour instability in the light. Rather and Beard (*Oil and Gas Journal*, 14.5.36, 209) showed that a kerosine which had gone off colour could be restored nearly to the original colour by the addition of hydroquinone in a suitable solvent. The proportion of the polyhydroxy benzenes such as hydroquinone, catechol or pyrogallol that was required was quite small. For example 1 lb. of hydroquinone dissolved in 1 gallon of a suitable solvent, such as *iso*propyl alcohol, could be mixed with 2,000 to 15,000 gallons of kerosine. The colour was removed by that treatment, but if intimately mixed with water the colour returned so that it looked as though an addition compound was formed from the hydroquinone and the colour-body in the kerosine. The discoloration process was associated with oxidation, as samples stored in an inert atmosphere in the absence of oxygen maintained their colour for a longer period than samples in the presence of air. A number of important papers on this subject appeared in the *Proceedings of the 1st World Petroleum Congress* (II) (708 *seq.*).

DR. DUNSTAN said that he also would like to congratulate Mr. Evans on his success in preparing such a meticulously careful summary of a chemically exasperating subject. One question had occurred to him which he thought the organic chemist would find of primary interest. If one considered the formula, for example, of ethylene, C_2H_4, one could write a complete thesis on the behaviour of that substance. One could calculate its boiling point, its density, its viscosity, and so forth, and could tell precisely what it would do under innumerable variations of chemical and physical conditions. One of the great boons that organic chemistry had conferred upon chemists was to demonstrate the relationship between structure and properties, *i.e.* between chemical constitution and properties. But the structure of large numbers of substances dealt with in the paper did not appear to be related in any way, as far as he could judge, with the particular physical properties that Mr. Evans had demanded; for instance, very specially the ability of the substances to improve the film strength of an oil. The question he wished to ask was this: Were the individual compounds mentioned in the paper related in any shape or form one to the other or to some desired fundamental definite physical property, or was the whole thing sheer empiricism from beginning to end? Was there any rhyme or reason in the selection of the reactants and the sort of substance that would be obtained? Had the substances been investigated from the point of view of modern molecular physical technique? Was it known, for example, whether the additive was concerned primarily with the lubricating oil or with the surface on which the lubricating oil was going to act? That was the kind of question which he would like Mr. Evans to discuss in detail.

MR. HAROLD MOORE, in congratulating Mr. Evans on his paper, said it was largely a compilation, and he thought a compilation was at least as valuable as experimental work. Personally he much preferred compilations, because they covered a larger field. He would like to suggest that Mr. Evans should collect all his data in a book, in which he might answer some of Mr. Dunstan's questions and try to explain the type of behaviour associated with the various substances with which he was dealing.

There was no mention in the paper of the paratone type of additive agent. Personally he knew only of paratone and a new product of the methacrylate type as agents for increasing viscosity and viscosity index. He would like to ask Mr. Evans whether he knew of other products for this purpose. He considered the viscosity increasing agents as of particular importance, perhaps even greater than the extreme pressure additives. The field for new viscosity raising additives appeared to be very open as probably many of the new plastics might serve this purpose if polymerized to the correct extent, both the paratone and the methacrylic acid being plastic polymers, and probably for the purpose of lubricating oil additives the polymerization was not carried as far as when making normal plastics.

He was very interested in Mr. Evans' reference to thioethers and to the compound phenthiazine, the anthracene type of structure containing a sulphur and NH group. He had recently tried out thianthrene, a compound possessing the same formula as anthracene in which the two middle carbons were substituted by sulphur atoms. It had been synthesized by the reaction of benzene with sulphur but he had not found it a satisfactory extreme pressure lubricant and its insolubility made it unsatisfactory as an anti-oxidant. As an extreme pressure lubricant he presumed the sulphurs were bound too tightly.

An interesting point in connection with synthetic work of this type was that the new process of aromatization enabled one to obtain pure samples of the higher aromatics containing 3, 4 or 5 benzene rings and they might form a very good basis for the preparation of compounds containing very heavy aromatic hydrocarbon groups. He wondered whether such heavy aromatic nuclei, perhaps containing sulphur or coupled up with other reactive groups, were likely to find a field in the preparation of additive agents.

DR. DUNSTAN asked which was the fundamental property that Mr. Moore wanted, length of side chain or total mass. He did not think the benzene rings *qua* benzene rings were any good.

MR. MOORE said that many of these bodies had naphthalene in them.

DR. DUNSTAN thought that some very useful information might be obtained from the modern chemical methods. For example the electron diffraction apparatus gave

a remarkably accurate picture of the lubricating oil molecule. Taking a very simple sort of substance, *e.g.* an ordinary fatty acid, it could be shown that the carboxyl group attached itself head first into the bearing surface and there remained a long hydrocarbon chain sticking up vertically like the pile of a carpet.

MR. W. J. KEMPTON said he thought that if one oxidized a transformer oil, for instance, it was only some of the oil molecules which took up the oxygen and then they acted as a catalyst to oxidize the rest of the molecules. That question had probably been discussed at previous meetings of the Institute, but he thought that, in dealing with the nucleus, it was well to realise that if one could stop the elementary oxidation one would probably hold back the whole reaction for the remaining amount of the oil. With regard to the way in which the inhibitor compounds in question were related to one another, it might be found that the relation was bound up with the preliminary oxidation being retarded, and that the products formed between inhibitor and oil were related one to another in the hydrogen carbon structure. He put this forward as a suggestion arising out of some work which he had done, but it was very difficult to separate many of the compounds, and one usually ended with emulsions and various products of which one could not determine the values.

DR. DUNSTAN said that the question mentioned by Mr. Kempton had been discussed by the Institute about twenty years ago, and the point had then been made that the lubricating oil *qua* lubricating oil was mainly a vehicle incorporating or containing a certain amount of reactive material, because the more thoroughly and completely the lubricating oil was refined the less reactive material one had, and hence the need for the additive.

MR. HAROLD MOORE said he had always been informed that the effect of the anti-oxidants was not to reduce the rate of oxidation throughout the entire period of oxidation but simply to delay oxidation by postponing the first attack of the oxygen, and that after the agent itself had been oxidized the oils underwent oxidation very much in the same way as if no agent had been present. He did not know whether this was in line with recent experience and he would like to know whether Mr. Evans had found the effect of anti-oxidants to be of that type, namely, the delay of preliminary oxidation afterwards followed by oxidation at the normal rate.

DR. DUNSTAN: You mean there is no permanent effect?

MR. MOORE: Yes.

DR. DUNSTAN: I think that is quite true.

MR. J. S. ELLIOTT, referring to what Professor Garner had said about lecithin, said that this material had been proposed recently for use in lubricating oils as an anti-oxidant with a fair amount of confidence. He had no knowledge as to whether or not it had been used in practice by the patentees. From his own laboratory experience he could say that it was effective in stabilising oil against oxidation, particularly at the lower temperatures, and that it reduced the deposition of insoluble matter and, to some extent, the rise in acidity consequent upon such oxidation.

With reference to the point raised by Dr. Dunstan about the relation between the effect of an addition agent and its structure, he realised that there was much yet to be learnt, but there seemed to be certain features which were common to the various groups of additives. Extreme pressure agents, for example, almost invariably contained either sulphur, chlorine, or phosphorus, the aim being to synthesize compounds containing these elements in a form readily available yet not unduly active. Among the sulphur compounds, for instance, it was considered desirable to load the molecule with as much sulphur as possible consistent with stability considerations, or alternatively to stimulate the activity of the sulphur by the introduction of other electro-negative radicals.

The reference to thianthrene was interesting, as although in this case the sulphur was too firmly bound to be of value, other useful substances could be prepared by analogous reactions involving the treatment of certain simple materials with sulphur or the sulphur chlorides. In many cases one could not tell exactly what the product would be like. As had already been pointed out, phenols reacted in chloroform solu-

tion with sulphur dichloride giving the corresponding di(hydroxyaryl) thioethers. If sulphur monochloride were used the product might be a disulphide (as from β-naphthol), or a mixture of thioether and free sulphur, or a mixture of thioether and trisulphide (as from *p*-chlorophenol), or even in some cases a mixture of thioether and tetrasulphide. Furthermore if free sulphur were added to the reaction mixture it could in certain cases be urged into chemical combination, a fair yield of di(*p*-chlorophenyl) trisulphide being obtainable from *p*-chlorophenol by this means. It was clear therefore that even such simple reactions as these required further study both for their own sake and in view of the possible usefulness of the products.

MR. E. A. EVANS, in replying to the discussion, said that Professor Garner had referred to the many types of compounds in use which were not mentioned in the paper, but he felt that 140 different patents were quite enough to deal with in one paper. He would like to remind the members present that the subject of additives was a very new one. A reference to the dates of the patents dealt with in the paper would show that very few of them were before 1935 and extraordinarily few before 1933, and it must be realized that there had been four years of war in which it had not been possible to do as much work on the subject as one would have liked to do. Therefore nearly all the development work had been done in about six years, clearly there was a great deal more to do before Dr. Dunstan's questions could be answered, as Dr. Dunstan himself knew.

Dr. Dunstan had asked whether there was any rhyme or reason in the selection of the reactants and the sort of substance that would be obtained. Different people had gone along different routes. Looking at the patents, it would be seen that one research organization had followed certain lines of thought, whilst another had followed other well-defined lines of thought. One school had dealt with phenols, another with amines, and yet another with thioethers. One school was paying much attention to the long-chain waxy compounds, whereas other chemists had decided to employ a shorter group such as *iso*propyl. The tendency at the present moment, he thought, was to employ the alkyl long-chain compounds, perhaps because they were more soluble. There was little doubt that such basic things as anthracene and phenanthrene would be useful He was giving that subject some thought and found that he was being led up a fairly interesting street. Questions of cost and solubility had to be considered. Some people had difficulty in making soluble compounds. This difficulty could sometimes be alleviated by the introduction of a long group. He thought that if some of the compounds mentioned in the paper were analysed with those thoughts in mind, it would be seen how some of the patentees had got over their stumbling-blocks.

It must be realized that the anti-oxidants had their own spheres of temperature. Some of them would act only up to 100 deg. C. and others only up to 80 deg. C., whilst others would do very well up to 150 deg. C., but would fail when put into an internal combustion engine, because the heat in the piston ring zone would cause them to break up. He did not think there was sufficient evidence to say how long the anti-oxidants would last; they were being used practically in power stations, and had been in continuous use for several years. There were better ones available now, which would last much longer than those which had been used in the past, and which would easily stand 150 deg. C. An anti-oxidant which would only stand 100 deg. C. might very well outstrip any of the others at that temperature.

THE PRESIDENT, in proposing a vote of thanks to Mr. Evans for his paper, said that the paper, with the discussion which had followed it and written contributions to the discussion which would probably be sent in later, would form a most valuable publication in the *Journal*.

The vote of thanks was accorded with acclamation, and the meeting then terminated.

CORRELATION OF I.P. LOVIBOND AND SAYBOLT CHROMOMETER COLOUR MEASUREMENTS ON MOTOR FUELS AND REFINED PETROLEUM.

Report by the Colour Panel of Standardization Sub-Committee 3.—*Liquefied Petroleum Gases, Gasoline, Kerosine, and Light Distillates.*

Two methods for determination of the colour of motor fuels and refined petroleum oils are described in Standard Methods for Testing Petroleum and its Products (1942 Edition)—namely, by the Lovibond Tintometer, using the 18-inch cell (method I.P.-17/42) and by the Saybolt Chromometer (method I.P.-18/42).

It is often desirable to be able to convert with approximate accuracy readings obtained on one instrument to the corresponding readings on the other.

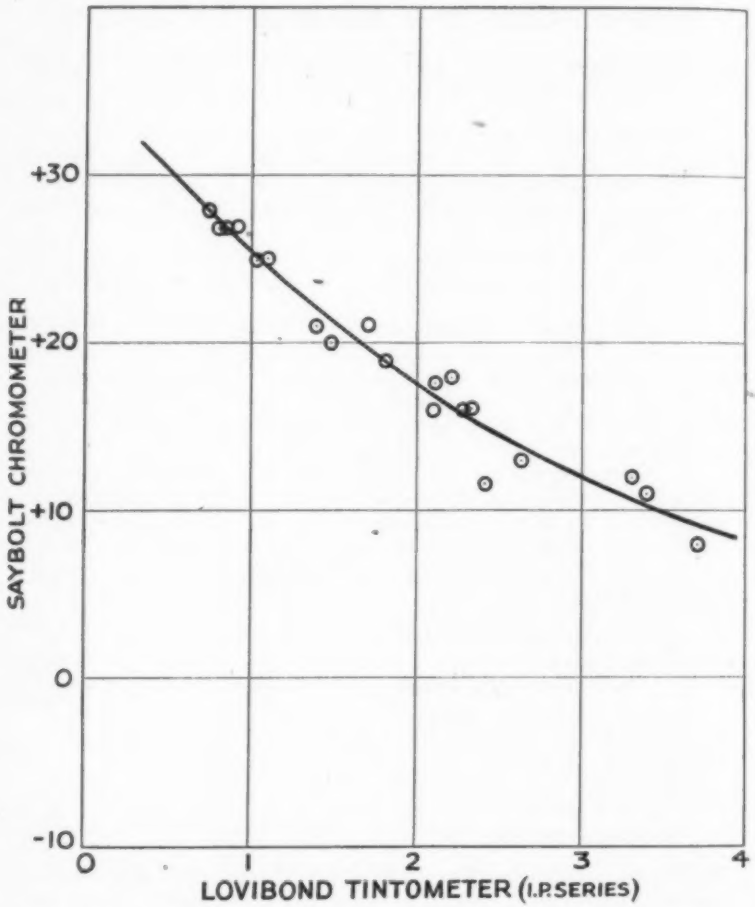
The standard glasses used in either the I.P. Lovibond or Saybolt instruments cannot be expected to match exactly, in regard to their primary colour composition, the colours of all petroleum products. This is particularly the case as the prevalent tints of motor fuels and kerosines may vary from time to time with changes in refining methods. No acceptable conversion curve for I.P. Lovibond and Saybolt readings being available, the Colour Panel of Sub-Committee No. 3 of the Institute of Petroleum Standardization Committee decided to carry out a series of determinations of colours by both methods on a range of typical products now available, using as many instruments and operators as were available to the Panel. The laboratories of the following organizations participated in the necessary experimental work :—

Anglo-American Oil Co., Ltd.
Burmah Oil Co.
Chemical Dept., H.M. Dockyard, Portsmouth.
Esso European Laboratories.
Imperial Chemical Industries.
National Benzole Co., Ltd.
Shell Refining & Marketing Co., Ltd.
The Tintometer, Ltd.
Trinidad Leaseholds, Ltd.

Twenty-two samples in all were circulated. They consisted of gasolines, kerosines, and benzoles, and were prepared by four of the co-operating laboratories. Every precaution was taken in preparing the samples, which were packed in glass bottles covered with paper to exclude light. To minimize any discrepancies which might have arisen from colour change in storage, the tests were carried out by all laboratories during pre-arranged periods of a few days, so that the time interval between dispatching and testing was substantially the same in all cases.

Eleven operators in all measured the colours of the samples by the

Saybolt Chromometer, and twenty-three operators carried out measurements with the Lovibond instrument using the I.P. Standard Glasses. The standard procedures (I.P. 17/42 and I.P. 18/42 respectively) were followed in all cases.



The tables below summarize the results obtained and record the mean results obtained on each sample by both instruments, together with the maximum variations from the means. The results on sample N.3 have been omitted from the curve showing the relationship between the mean values. The colour of this particular sample is not suitable for comparison with the standard glasses used for refined petroleum.

SAYBOLT CHROMOMETER.

Sample.	A.	B.	C.	D.	E.	F.	G.	N1.	N2.	N3.	S1.	S2.	S3.	S4.	S5.	S6.	A2.	B2.	C2.	D2.	E2.	F2.
Average Colour . . .	+27	17·6	11·6	28	19	16	8	+27	+16	Zero	+27	+25	+16	+21	+20	+12	+11	+18	+13	+21	+25	+16
Diff. from Lowest . .	− 1	−0·6	−0·6	−2·0	−1·0	−1·0	−3·0	− 2	− 1	− 5	− 1	− 2	− 2	− 3	− 1	− 4	− 3	− 2	− 3	− 2	− 3	− 3
Average Highest . .	+ 1	+0·4	+1·4	+1·0	+1·0	+1·0	+2·0	+ 1	+ 2	+ 4	+ 2	+ 2	+ 2	+ 1	+ 2	+ 2	+ 3	− 2	+ 4	+ 2	+ 2	+ 2

LOVIBOND (I.P. SERIES) (18" CELL).

Sample.	A.	B.	C.	D.	E.	F.	G.	N1.	N2.	N3.	S1.	S2.	S3.	S4.	S5.	S6.	A2.	B2.	C2.	D2.	E2.	F2.
Average Colour . . .	0·83	2·1	2·4	0·75	1·8	2·3	3·7	0·81	2·09	2·96	0·90	1·07	2·09	1·69	1·46	3·29	3·39	2·2	2·62	1·39	1·02	2·82
Diff. from Lowest . .	0·58	0·60	0·15	0·50	0·80	0·30	0·95	0·31	0·09	0·46	0·40	0·57	0·59	0·69	0·46	1·04	0·89	0·70	0·37	0·39	0·52	0·82
Average Highest . .	0·17	0·15	0·35	0·25	0·45	0·45	0·30	0·19	0·16	0·04	0·10	0·43	0·16	0·31	0·04	0·71	0·61	0·05	0·88	0·61	0·48	0·43

It will be seen from the results that a very reasonable correlation has been obtained. The relationship should be of use in making approximate conversions for comparative purposes, but it must again be emphasized that as colour measurements of this kind are based on comparison with arbitrarily selected standards, conversion with a high degree of accuracy is not possible.

In carrying out correlation work of this kind it became obvious that certain precautions were very necessary and should always be observed in connection with colour measurements. These precautions may be summarized as follows, and apply more particularly to the Lovibond instrument.

1. Operators should be tested for colour perception. The eyesight of all laboratory workers is not suitable for this work.
2. Fatigue of the eye should be avoided. Only a few observations should be made at a time; a series of short confirmatory observations is better than prolonged gazing at a colour.
3. Tests should be made in a room with diffused white light.
4. The least number of glasses possible to obtain the correct value should be used.
5. Apparatus should be properly set up and a clear field of view obtained in the eyepiece. The cell should be so placed that no part of the sides or end is visible in either mirror.
6. Apparatus should be kept scrupulously clean, attention being given to white reflecting opal screen, colour glasses, mirrors, and white internal paint in the light cabinet.

DEFINITIONS FOR WAXES, ETC., DERIVED FROM PETROLEUM.

Report by the Nomenclature Panel of Standardization Sub-Committee No. 8.—Petroleum Waxes.

Introduction.

(1) The term "petroleum wax" has been chosen to comprehend all waxes derived from petroleum, and the attached diagram illustrates the relationship of the various products. Petroleum waxes are divided, mainly on the basis of crystal size, consistency, and method of manufacture, into three groups: the "paraffin wax" group, the "petrolatum" group, and the "petroleum ceresin" group. The two latter groups include waxes previously classed as "microcrystalline" or "amorphous." The current use of these terms is, however, so loose and erroneous as to make their abandonment advisable.

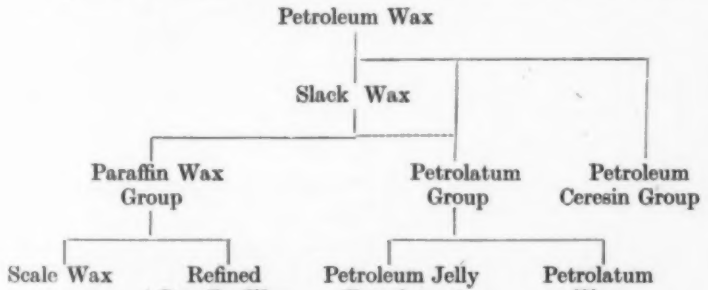
"Slack wax" is shown on the diagram as a petroleum wax, but is nevertheless placed outside the three groups. It is intended to indicate that the term is usually applied to an oil–wax mixture in which the wax is of the paraffin-wax group. The term is, however, not restricted to this application.

(2) The definitions are intended for petroleum products, but it is common practice to apply the same terms to comparable products from shale, etc.

(3) Descriptions of consistency, etc., throughout the definitions refer to characteristics at ordinary temperatures.

(4) Natural or artificial mixtures of these classes and sub-classes may be met (*e.g.*, a mixture of petroleum ceresin, petrolatum wax, and refined paraffin wax). In view of this, caution must be exercised in applying the classification, particularly as the petroleum ceresins have the power of conferring in some degree their small crystal size on paraffin waxes, thereby destroying the characteristic structure of the latter.

Diagram to Illustrate the Relationship of the Products Considered.



DEFINITIONS.

Petroleum Wax.

Wax-like materials, derived from petroleum, comprised of normal and branched paraffins and possibly hydrocarbons of other series. Molecular weight ranges from about 225 to 1000, and setting point from about 60° F. to 220° F. Consistency may be soft, semi-solid, or solid, and crystal size and form may vary widely.

Slack Wax.

Mixtures of crude petroleum wax and oil, usually obtained by separation from waxy oil. Consistency may be soft or semi-solid, and oil content is normally from 10 to 50 per cent. The term is usually applied to distillate products.

Oil in Wax.

Oil in wax can be defined only in relation to temperature, and is that part of an oil–wax mixture which is liquid at a specified temperature.

Note.—This definition can be made more precise only when a method for estimating oil in wax has been standardized.

Group I—Paraffin Wax Group.

Petroleum waxes, derived from distillates, comprised mainly of normal paraffins, of solid consistency, and having a relatively pronounced crystalline structure. Molecular weight ranges from about 225 to 450, and they have setting points up to about 160° F.

The paraffin wax group is sub-divided, mainly on the basis of oil content, into (*a*) scale wax and (*b*) refined paraffin wax.

(*a*) *Scale Wax.*—Paraffin wax, usually obtained by the process of sweating the greater part of the oil from slack wax. Scale wax contains up to 10 per cent. of oil, and is often a crumbly solid. Setting points range from about 90° to 140° F.

(*b*) *Refined Paraffin Wax.*—Paraffin wax of very low oil content, highly refined, white, with some degree of translucency, almost tasteless and odourless, and not more than slightly greasy to the touch. Setting points range from about 90° to 160° F.

Group II—Petrolatum Group.

Petroleum waxes, derived mainly from distillation residues, and varying in consistency from salve-like to solid and plastic. They vary in colour from dark brown to white. Molecular weight is usually over 450, and setting point ranges from about 100° to 180° F. They contain considerable quantities of hydrocarbons other than normal paraffins, and waxes of this group are nearly always of smaller crystal size than those of the paraffin wax group.

The petrolatum group is sub-divided, mainly on the basis of oil content into (*a*) petrolatum wax and (*b*) petroleum jelly.

(*a*) *Petrolatum Wax.*—Petrolatum, solid and plastic, substantially free from oil, and possessing some degree of tackiness. The setting point, which is often indistinct, is generally below 180° F.

(*b*) *Petroleum Jelly* (*Petrolatum*).—Petrolatum, soft and salve-like, consisting of certain petrolatum waxes in admixture with a substantial proportion of oil.

Note.—For the purpose of this classification the term "petroleum jelly" is preferred to "petrolatum," so as to avoid possible confusion with "petrolatum wax."

Group III—Petroleum Ceresin Group.

Petroleum waxes, usually derived from distillation residues, essentially free from oil, and hard and brittle. They vary in colour from dark brown to white. Molecular weight ranges from about 450 to 1000, and the setting point is usually above 160° F. Generally the crystal size is much smaller than that of paraffin wax. Their hydrocarbon constitution is at present obscure.

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WAR-TIME SPECIFICATION FOR I.P. PETROLEUM HYDROMETERS

A war-time specification for hydrometers has been prepared by the Standardization Committee in close collaboration with representatives of the manufacturers. The complete specification is printed below, prior to publication in the next edition of " Standard Methods," so that the new hydrometers can come into use immediately. Instruments conforming to the 1935 and 1942 specifications may still be used, but, in future, hydrometers manufactured in accordance with this war-time specification will be generally acceptable.

Under the restrictions imposed by war-time conditions manufacturers have experienced considerable difficulty in maintaining the required output, and it has frequently happened that time and material have been wasted as the result of instruments failing to meet stringent dimensional requirements which were not absolutely essential for the production of accurate hydrometers.

Wherever possible, the more stringent dimensional requirements have therefore been relaxed. Thus it will be seen that the obligatory specification includes the overall length, the length of scale, and the minimum length of stem below the bottom graduation, in addition to the accuracy clause. It is hoped that these war-time specifications will ensure that the best use is made of available material and labour, and it will be noted that while relaxing the dimensional requirements, it has been considered reasonable to stipulate rather greater accuracy than was demanded in the 1942 specifications.

The war-time specification aims at the highest standards in all essentials, while removing unduly restrictive dimensional requirements.

In connection with these war-time hydrometers, it will be appreciated that certification by the National Physical Laboratory will refer essentially to the accuracy of the instruments when used for petroleum products.

WAR-TIME I.P. PETROLEUM HYDROMETERS

Hydrometers shall conform to the dimensions given in Table I (p. 4) and to the following specification:—

(i) Hydrometers shall be made of glass, free from striæ or similar defects, and in particular the external surface of the stem shall be quite smooth. The glass shall be resistant to the action of chemicals and possess properties such as would render it suitable for use for thermometers; *i.e.*, it should have low thermal hysteresis and small secular change in volume.*

(ii) Hydrometers shall be thoroughly annealed before the scale is fixed.

(iii) For ranges above 0·700, the main bulb shall be cylindrical and/or torpedo-shaped (cylindrical for the greater part of its length and terminating in a cone), whilst for ranges below 0·700 it may be of any suitable shape. In all cases the cross-section of the stem shall be circular.

(iv) A thermometer shall not be part of the instrument.

(v) When mercury is used for loading, it is to be contained in a bulb at the base of the hydrometer, suitably sealed off with glass from the main bulb of the instrument.

(vi) In special hydrometers for use at higher temperatures than 100° F. any material used for sealing off the bulb or for holding loading material, such as shot, shall not soften below 212° F. (All hydrometers, after use at a higher temperature than 100° F., shall, as a matter of precaution, be allowed to drain and cool in a vertical position.)

(vii) The hydrometer shall be symmetrically constructed so that it floats with the stem vertical.

(viii) Paper of high quality shall be used for the scale, conforming with the requirements that it does not discolour at 212° F. with use and that all divisions may be sharply and accurately marked on it.

(ix) The scale shall be straight and without twist, and fixed with a cement which will not soften at the highest temperatures at which the hydrometer may be used.

(x) The scale of each hydrometer shall be graduated at each end for four divisions beyond its nominal range in Type 1, for two divisions in Type 2 and for one division in Type 3.

(xi) The graduation marks shall be made by fine straight lines, which lie in planes perpendicular to the axis of the hydrometer, so that the graduation marks are horizontal when the stem is vertical.

(xii) The subdivisions of the scale shall be without evident irregularities.

(xiii) Every 0·05 graduation mark shall be numbered without inserting either the decimal point or the figure 0 preceding the

* During the present war emergency, good quality glass other than of thermometric type may be used.

decimal point. The first one (or two) of the figures shall appear to the left of the scale and the last two to the right, *e.g.*, 6–50 and 7–00; 9–50 and 10–00. In addition, every intermediate 0·01 graduation mark shall be numbered, but abbreviated numbers shall be used for this purpose, *e.g.*, 60, 70, etc. These abbreviated numbers shall be printed on the right of the scale.

(xiv) The length of the graduation marks must be varied so that the exact reading corresponding to any mark can be easily identified. The shortest graduation marks must be at least 2 mm. in length.

(xv) A fine horizontal line shall be etched on the stem of the hydrometer Types 1 and 2, and this shall coincide with the horizontal part of a " pointing mark " which shall be ruled on the paper scale about 5 mm. above the highest graduation. This " pointing mark " shall be a short, fine line with a V at each end, thus:

(xvi) All hydrometers shall be graduated for reading correctly at the point of intersection of the level liquid surface with the stem.

(xvii) Hydrometers must be adjusted so that the reading on the scale in a liquid whose temperature is 60° F., which, in the case of Type 1 and Type 2 hydrometers, has the appropriate surface tension as given below, gives the specific gravity of the liquid at 60° F. relative to water at 60° F. (sp. gr. 60° F./60° F.).*

Hydrometer ranges.	Surface tension.
0·650 to 0·700 and 0·700 to 0·750	20 dynes/cm.
0·750 to 0·800 and 0·800 to 0·850	25 "
0·850 to 0·900 and 0·900 to 0·950	30 "
0·950 to 1·000, 1·000 to 1·050 and 1·050 to 1·100	35 "

The specific gravity 60° F./60° F. of water* shall be taken as 1·000 and the scale numbered accordingly.

(xviii) The maker shall mark each hydrometer with:

(*a*) " S $\frac{60° \text{ F.}}{60° \text{ F.}}$ at 60° F.," to indicate the basis of the scale.

(*b*) " Petroleum."

(*c*) " I.P. Type . . . " and an identification number.

(*d*) Vendor's or maker's name or mark.

(*e*) " Max. Temp. 212° F." or " Max. Temp. 100° F." according to whether the cementing material for fixing the loading is or is not suitable for the hydrometer to be used above 100° F.

* Specific gravity is defined as the ratio of the mass of a given volume of the product at a temperature t_1 to the mass of an equal volume of pure water at a temperature t_2. The masses are compared by weighings in air using brass weights and correcting to the corresponding weights *in vacuo*.

$$\text{Sp. Gr.} \frac{60° \text{ F.}}{60° \text{ F.}} = \frac{\text{Mass of a given volume of the substance at 60° F.}}{\text{Mass of an equal volume of water at 60° F.}}.$$

Three series of hydrometers, covering a range in each series of 0·650–1·100 specific gravity, have been adopted. Each series consists of ten separate instruments, each having a range of specific gravity of 0·05, as follows:

0·600 to 0·650	0·850 to 0·900
0·650 to 0·700	0·900 to 0·950
0·700 to 0·750	0·950 to 1·000
0·750 to 0·800	1·000 to 1·050
0·800 to 0·850	1·050 to 1·100

When extreme accuracy is required, or in referee work, instruments certified by the National Physical Laboratory for accuracy shall be used. The corrections shown on the accompanying certificate shall be applied.

TABLE I.

Specified Dimensions and Tolerances.

	Type 1.	Type 2.	Type 3.
Length overall, mm.	Max. 360 Min. 330	Max. 240 Min. 210	Max. 180 Min. 160
Number of sub-divisions in nominal scale	100	50	50
Length of nominal range of scale, mm.	Max. 185 Min. 155	Max. 115 Min. 90	Max. 65 Min. 50
Length of plain cylindrical stem below bottom graduation mark, mm.	Min. 5	Min. 5	Min. 5
Maximum permissible error at any point on the scale	±0·0003	±0·0005	±0·001

The further dimensions shown in Table II are not to be regarded as obligatory, but merely as indicating the types of instruments desired.

TABLE II.

Recommended Dimensions and Tolerances.

	Type 1.	Type 2.	Type 3.
Diameter of bulb, mm.	Max. 40 Min. 35	Max. 25 Min. 20	Max. 20 Min. 16
Diameter of stem, mm.	Min. 5·0	Min. 4·3	Min. 4·0
Distance of top nominal graduation mark from top of stem, mm.	Min. 25	Min. 15	Min. 10

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